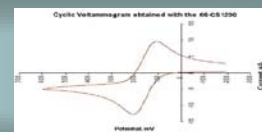


## Analytical Electrochemistry: The Basic Concepts



### a) Linear Sweep Voltammetry

In a previous section, we presented the diffusion controlled current-time behavior of a redox couple following a step to a potential sufficient to reduce all of the electroactive species near the surface of the electrode. Faradaic current was observed to decay as a function of  $t^{-1/2}$  according to the Cottrell equation. This was explained in terms of the concentration profile extending from the electrode surface into the bulk of solution. The thickness of this diffusion layer increases with time, decreasing the slope of the concentration gradient, and thus reducing the observed current.

We must now consider what happens to the concentration of electroactive species near the electrode as the potential is scanned, rather than stepped. Instead of going immediately to zero, the concentration of Ox is now dependent on the magnitude of the applied potential with respect to the  $E^0$ , with the ratio of  $C_{\text{Red}}$  to  $C_{\text{Ox}}$  (at 25 °C) given by the Nernst equation

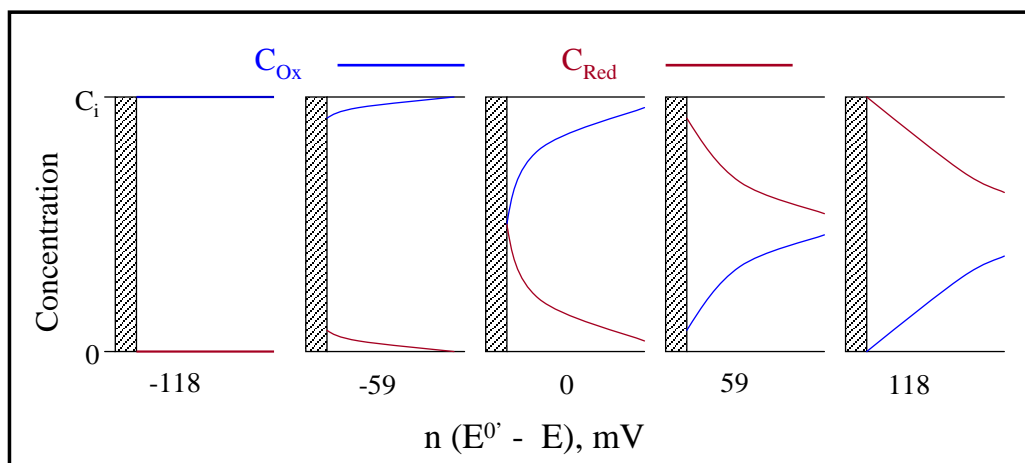
$$E = E^0 - (0.059 / n) \log [C_{\text{Red}} / C_{\text{Ox}}]$$

For our discussion, it is convenient to express the applied potential,  $E$ , in terms of its proximity to  $E^0$ , rearranging the Nernst equation as follows

$$\frac{n (E^0 - E)}{0.059} = \log \frac{C_{\text{Red}}}{C_{\text{Ox}}}$$

The concentration gradients existing for Ox and Red at several values of  $[n (E^0 - E)]$  are illustrated in **Figure 15** ( $0.059 \text{ V} = 59 \text{ mV}$ ).

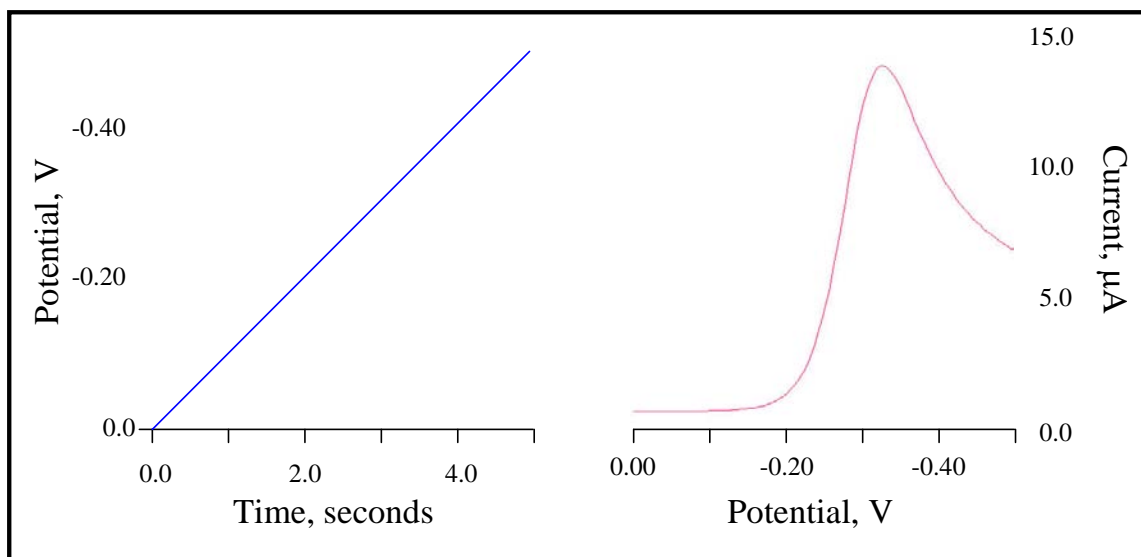
**Figure 15**



For a 1-electron reduction under diffusion control with an applied potential 118 mV positive of the  $E^{0'}$ ,  $C_{Ox} = 100 C_{Red}$  at the electrode surface. A potential 59 mV positive of the  $E^{0'}$  yields  $C_{Ox} = 10 C_{Red}$ . When the applied potential equals the  $E^{0'}$ ,  $(E^{0'} - E) = 0$ , and the two concentrations are equal adjacent to the electrode, with each being half of the initial, or bulk concentration of  $C_{Ox}$  ( $C_i$  in **Figure 15**). Beyond the  $E^{0'}$ , the concentration of  $C_{Red}$  becomes larger than that of  $C_{Ox}$ , with  $C_{Red} = 10 C_{Ox}$  at a point 59 mV more negative than the  $E^{0'}$ , and  $100 C_{Ox}$  at a point 118 mV more negative.

An important difference in the concentration gradients for potential sweep experiments when compared to large potential step experiments is that the slope of the gradient is dependent upon *both* the  $C_{Ox}$  at the electrode surface (non-zero in the vicinity of  $E^{0'}$ ) and the thickness of the diffusion layer, not just the latter. A consequence of this is that the maximum concentration gradient (and hence maximum current) is observed at a potential 28.5 mV (for  $n = 1$ ) beyond the  $E^{0'}$  of the redox couple. The *potential – time* and *current – potential* curves are presented in **Figure 16** for a 1-electron, diffusion controlled redox couple with an  $E^{0'}$  of -0.300 V. The rate at which the potential is scanned is called the *scan rate* (big surprise) and is represented by  $\nu$ , generally with units of V/s. The *initial potential* is 0.00 V, with the *final potential* equal to -0.50 V. The current decrease beyond the peak potential (-0.328 V) is the result of  $C_{Ox}$  at the electrode surface being driven to zero and the extension of the diffusion layer further and further into solution as the scan continues. (DigiElch simulation parameters:  $\nu = 0.100$  V/s;  $A = 0.050$  cm<sup>2</sup>;  $C_i = 1.0$  mol/cm<sup>3</sup>;  $D = 1.0 \times 10^{-5}$  cm<sup>2</sup>/s;  $\alpha = 0.50$ ;  $k_s = 100$  cm/s)

**Figure 16**



The observed peak current,  $i_p$ , for a reversible electron transfer in LSV is given by the Randles-Sevcik equation

$$i_p = (2.69 \times 10^5) n^{3/2} A D^{1/2} C_i \nu^{1/2}$$

where  $2.69 \times 10^5$  is a collection of constants at 25 °C, and the variables are as previously defined. The capacitive current, which appears as the non-zero baseline at the left of the current-

potential scan, must be subtracted from the total current to correctly obtain  $i_p$ . Most commercial instrumentation allows for this to be done digitally.

LSV can be used to determine such parameters for a reversible system as  $E^{0'}$ ,  $n$ ,  $D$ , and  $C_i$ , while the use of a known redox couple can be employed in the calculation of  $A$ . As we have seen, the  $E^{0'}$  value occurs at a point  $(28.5/n)$  mV positive (for a reduction) of the observed peak potential,  $E_p$ . If difficulty is experienced with the accurate location of a peak potential, the potential measured at half the peak height ( $E_{p/2}$ ) can be used to calculate it, lying  $(56.5/n)$  mV more positive than the  $E_p$  (for a reduction). If a value for  $D$  is known, the  $n$ -value for a redox active species can be calculated using the Randles-Sevcik equation. In most cases, even  $D$  values estimated from similar structures with known diffusion coefficients will suffice.

A plot of peak current,  $i_p$ , as a function of  $v^{1/2}$ , is linear for a redox active species under diffusion control, and can be a useful diagnostic indicator for a redox system being characterized for the first time. For reversible electron transfer, the position of  $E_p$  will not change with scan rate. The separation between  $E_{1/2}$  and  $E_p$  can also be used to diagnose reversible electron transfer, with  $|E_p - E_{p/2}|$  equal to  $(56.5/n)$  mV for a reversible electron transfer ( $k_s > 0.02$  cm/s). For irreversible electron transfer ( $k_s < 5 \times 10^{-5}$  cm/s),  $|E_p - E_{p/2}|$  will equal  $(47.7/\alpha n)$  mV. Intermediate values for  $k_s$ , defining the quasi-reversible regime, will yield intermediate values for  $|E_p - E_{p/2}|$  as well.